5   **PROCESS FOR THE PRODUCTION OF AN OLEFIN OXIDE**

FIELD OF THE INVENTION

       The present invention relates to a process for the

10   production of an olefin oxide, a 1,2-diol, a 1,2-diol

ether or an alkanolamine.

BACKGROUND OF THE INVENTION

       In olefin epoxidation an olefin is reacted with

oxygen to form an olefin epoxide, using a catalyst

15   comprising a silver component, usually with one or more

further elements deposited therewith on a support. The

olefin oxide may be reacted with water, an alcohol or an

amine to form a 1,2-diol, a 1,2-diol ether or an

alkanolamine. Thus, 1,2-diols, 1,2-diol ethers and

20   alkanolamines may be produced in a multi-step process

comprising olefin epoxidation and converting the formed

olefin oxide with water, an alcohol or an amine.

       The performance of the epoxidation process may be

assessed on the basis of the selectivity, the catalyst's

25   activity and stability of operation. The selectivity is

the molar fraction of the converted olefin yielding the

desired olefin oxide. The catalyst is subject to an

ageing-related performance decline during normal

operation. The ageing manifests itself by a reduction in

30   the activity of the catalyst. Usually, when a reduction

in activity of the catalyst is manifest, the reaction

temperature is increased in order to compensate for the

reduction in activity, however at the expense of

selectivity. In the typical operation of a fresh

35   catalyst, the process is operated at a reaction

temperature of at most 255 °C. Upon catalyst ageing the

reaction temperature may gradually be increased to values

substantially above 255 °C until the reaction temperature
becomes undesirably high, at which point in time the
catalyst is deemed to be at the end of its lifetime and
would need to be exchanged. It goes without saying that

5   from an economical point of view it is highly desirable
to improve the performance of the catalyst and to extend
its lifetime as much as possible. Quite modest
improvements in the maintenance of selectivity over long
periods yields huge dividends in terms of efficiency in

10   the olefin epoxidation process and, if applicable, also
in the overall process for the production of a 1,2-diol,
a 1,2-diol ether or an alkanolamine.

     Therefore, for decades much research has been devoted
to improving the activity, the selectivity and the

15   lifetime of the catalysts, and to find process conditions
which enable to fully exploit the catalyst performance.
     An organic halide, for example a chlorohydrocarbon,
may be added to the feed to an epoxidation reactor as a
reaction modifier for increasing the selectivity. The

20   reaction modifier suppresses the undesirable oxidation of
olefin or olefin oxide to carbon dioxide and water,
relative to the desired formation of olefin oxide.

     US-A-4766105 and US-A-4761394 disclose that rhenium
may be employed as a further element in the silver-

25   containing catalyst with the effect that the selectivity
of the olefin epoxidation is increased.

     US-B-6372925 and WO-01/96324 teach that when
operating with a catalyst which exhibits an improved
selectivity, for example a catalyst known from US-A-

30   4766105 or US-A-4761394, it is advantageous to increase
the ethylene content of the feed when the catalyst has
reached a certain stage of ageing. The increased
ethylene content substantially improves the selectivity
of the conversion of ethylene into ethylene oxide.

Not withstanding the improvements already achieved, there is a desire to further improve the performance of the silver-containing catalysts in the production of the production of an olefin oxide, a 1,2-diol, a 1,2-diol

5   ether or an alkanolamine.

SUMMARY OF THE INVENTION

The present invention provides a process for the production of an olefin oxide, which process comprises reacting a feed comprising an olefin and oxygen in the

10   presence of a supported silver-containing catalyst, wherein before the catalyst has reached an advanced stage of ageing the reaction temperature is above 255 °C and the olefin content of the feed is above 25 mole-%, relative to the total feed.

15   The invention also provides a process for the production of an olefin oxide, which process comprises reacting a feed comprising an olefin and oxygen at a reaction temperature above 255 °C and an olefin content of the feed above 25 mole-%, relative to the total feed, in

20   the presence of a silver-containing catalyst which has not reached an advanced stage of ageing.

The invention also provides a method of using an olefin oxide for making a 1,2-diol, a 1,2-diol ether or an alkanolamine comprising converting the olefin oxide

25   into the 1,2-diol, the 1,2-diol ether or the alkanolamine, wherein the olefin oxide has been obtained by the process according to this invention.

DETAILED DESCRIPTION OF THE INVENTION

In accordance with this invention, when a fresh

30   catalyst is used at a relatively high temperature, i.e. above 255 °C, the performance of the catalyst, in particular the activity, the selectivity, and the ageing related performance decline, are improved when the olefin content of the feed is increased. Such improvements have

not become apparent when the catalyst was used at a relatively low temperature.

This is unobvious over the teachings of US-B-6372925 and WO-01/96324. These documents show the performance of

5   fresh catalysts at their typical use temperature of at most 255 °C and the performance of aged catalysts at their typical use temperature of above 255 °C. These documents are silent about the performance of fresh catalysts at reaction temperatures above 255 °C.

10 As used herein, "an advanced stage of ageing" of the catalyst is defined by a cumulative olefin oxide production of at least 10,000 kmole, in particular at least 5000 kmole, more in particular at least 2000 kmole, most in particular at least 1000 kmole, of olefin oxide

15 per m^3 of catalyst bed. As used herein, "fresh catalyst" means a catalyst immediately after its preparation or rejuvenation, or a catalyst which, in the course of operation, has not yet reached an advanced stage of ageing.

20 Although the present epoxidation process may be carried out in many ways, it is preferred to carry it out as a gas phase process, i.e. a process in which the feed is contacted in the gas phase with the catalyst which is present as a solid material, typically in a packed bed.

25 Generally the process is carried out as a continuous process.

The olefin for use in the present epoxidation process may be any olefin, such as an aromatic olefin, for example styrene, or a di-olefin, whether conjugated

30 or not, for example 1,9-decadiene or 1,3-butadiene. Typically, the olefin is a monoolefin, for example 2-butene or isobutene. Preferably, the olefin is a mono-α-olefin, for example 1-butene or propylene. The most preferred olefin is ethylene.

The olefin content of the feed is above 25 mole-%, typically at least 30 mole-%, more typically at least 35 mole-%, relative to the total feed. Typically the olefin content of the feed is at most 80 mole-%, more typically

5   at most 70 mole-%, relative to the total feed. In preferred embodiments, amongst others, the olefin content of the feed is maintained at a value of at least 25 mole-%, typically at least 30 mole-%, more typically at least 35 mole-%, relative to the total feed, when the catalyst

10   has reached an advanced stage as ageing. Also at an advanced stage of ageing the olefin content of the feed is typically at most 80 mole-%, more typically at most 70 mole-%, relative to the total feed. Typically the olefin content of the feed is maintained at the value as

15   defined for at least a period which is sufficient to effect an olefin oxide production of at least 1000 kmole, more typically at least 5000 kmole, most typically at least 10,000 kmole, of olefin oxide per m^3 catalyst bed, preferably up to the end of the catalyst's lifetime, that

20   is when the catalyst will be exchanged and/or rejuvenated. As used herein, the feed is considered to be the composition which is contacted with the catalyst.

The direct oxidation of an olefin to the corresponding olefin oxide can be air-based or oxygen-

25   based, see Kirk-Othmer's *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 9 (1980) p. 445-447. In the air-based processes air or air enriched with oxygen is fed directly to the system while in the oxygen-based processes high-purity (above 95 mol-%) oxygen is employed

30   as the source of the oxidizing agent. Presently most ethylene oxide production plants are oxygen-based and this is the preferred embodiment of the present invention.

The oxygen content of the feed is within the broad range of from 3 to 20 mole-%, preferably from 5 to 12 mole-%, relative to the total feed.

In order to remain outside the flammability limit of
5   the reaction mixture, the oxygen content of the feed is usually balanced with the olefin content. The actual safe operating ranges depend, along with the gas composition (reactants and balance gases), also on individual plant conditions such as temperature and
10 pressure.

In addition to the olefin and oxygen, the feed may contain one or more optional components, such as carbon dioxide, a reaction modifier and balance inert gases.

Carbon dioxide is a by-product of the olefin
15 oxidation process. Since frequently unconverted olefin is continuously recycled, and since a content of carbon dioxide in the feed which is much in excess of 15 mole-% will have an adverse effect on catalyst activity, accumulation of carbon dioxide will be avoided by
20 continuously removing carbon dioxide from the recycle gas. This may be done by venting and by continuous absorption of the formed carbon dioxide. Currently contents of carbon dioxide as low as 1 mole-% are practical, for example in the range of from 0.5 to
25 1 mole-%, and in future even lower contents may be reached. The process of the present invention is independent of the presence or absence of carbon dioxide in the reaction mixture.

A reaction modifier may be added to the feed for
30 increasing the selectivity, suppressing the undesirable oxidation of olefin and of the olefin oxide to carbon dioxide and water. Many organic compounds, especially organic halides but also amines, organometallic compounds and aromatic hydrocarbons are known to be effective in

this respect.   Organic halides are the preferred reaction
modifiers and they are effective without suppressing the
desired reaction when used in quantities ranging from 0.1
to 25 parts per million by volume (ppmv), in particular

5   from 0.3 to 20 ppmv, relative to the total feed.
Dependent of the silver-containing catalyst employed, the
reaction modifier content of the feed may be optimized
from time to time during operation if the maximum
achievable selectivity is to be maintained.   Preferred

10   organic halides are C_1 to C_8 chlorohydrocarbons or
bromohydrocarbons.   More preferably they are selected
from the group of methyl chloride, ethyl chloride,
ethylene dichloride, ethylene dibromide, vinyl chloride
or a mixture thereof.   Most preferred reaction modifiers

15   are ethyl chloride and ethylene dichloride.

The balance inert gases usually present in the feed
comprise, for example, nitrogen, argon, and/or saturated
hydrocarbon such as methane or ethane. When unconverted
olefin is continuously recycled, and oxygen added, the

20   accumulation of balance gases is avoided.   The process of
the present invention is independent of the amount of
balance inert gases in the reaction mixture.

"GHSV", or Gas Hourly Space Velocity, is the unit
volume of gas at standard temperature and pressure (0 °C,

25   1 atm, i.e. 101.3 kPa) passing over one unit volume of
packed catalyst per hour.   Preferably, if the process is
carried out as a gas phase process, the GHSV is in the
range of from 1500 to 10000.   The reactor inlet pressure
is preferably in the range of from 1000 to 3500 kPa.

30   The reaction temperature is typically at least 260 °C,
more typically at least 265 °C, most typically at least
270 °C.   The reaction temperature is typically at most
325 °C, more typically at most 310 °C.   In preferred
embodiments, amongst others, the reaction temperature is

maintained at a value of above 255 °C, typically at least 260 °C, more typically at least 265 °C, most typically at least 270 °C when the catalyst has reached an advanced stage of ageing. Also at an advanced stage of ageing the

5   reaction temperature is typically at most 325 °C, more typically at most 310 °C. Typically the reaction temperature is maintained at the value as defined for at least a period which is sufficient to effect an olefin oxide production of at least 1000 kmole, more typically

10   at least 5000 kmole, most typically at least 10,000 kmole, of olefin oxide per m^3 catalyst bed, preferably up to the end of the catalyst's lifetime, that is when the catalyst will be exchanged and/or rejuvenated.

15   The present process may be started-up by using procedures known in the art, for example from US-A-4874879 and US-5155242, which are incorporated herein by reference. After passing the start-up phase, and at some point in time before the catalyst has reached an advanced

20   stage of ageing, the catalyst may be subjected to the conditions of reaction temperature and olefin content of the feed as defined in accordance with this invention, until the catalyst has reached an advanced stage of ageing. In this context, the stage of ageing of the

25   catalyst is considered on the basis of the total quantity of olefin oxide produced, that is including for example the olefin oxide production, if any, during the start-up procedure.

        The material of the support of the supported silver-

30   containing catalysts may be selected from a wide range of conventional materials which are considered to be inert in the presence of the olefin oxidation feed, products and reaction conditions. Such conventional materials can be natural or artificial and they may include aluminum

oxides, magnesia, zirconia, silica, silicon carbide, clays, pumice, zeolites and charcoal. Alpha alumina is the most preferred material for use as the main ingredient of the porous support.

5   The support is typically porous and has preferably a surface area, as measured by the B.E.T. method, of less than 20 m^2/g and more in particular from 0.05 to 20 m^2/g. Preferably the B.E.T. surface area of the support is in the range of 0.1 to 10, more preferably from 0.1 to 3.0

10   m^2/g. The B.E.T. method of measuring the surface area has been described in detail by Brunauer, Emmet and Teller in *J. Am. Chem. Soc.* 60 (1938) 309-316.

The catalyst comprises silver as a catalytically active metal. Appreciable catalytic activity is obtained

15   by employing a silver content of the catalyst of at least 10 g/kg, relative to the weight of the catalyst. Preferably, the catalyst comprises silver in a quantity of from 50 to 500 g/kg; more preferably from 100 to 400 g/kg, relative to the weight of the catalyst.

20   The catalyst preferably comprises, in addition to silver, a further element or compound thereof. Eligible further elements may be selected from the group of nitrogen, sulfur, phosphorus, boron, fluorine, Group IA metals, Group IIA metals, rhenium, molybdenum, tungsten,

25   chromium, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the Group IA metals are selected from lithium, potassium, rubidium and cesium. Most preferably the Group IA metal is lithium,

30   potassium and/or cesium. Preferably the Group IIA metals are selected from calcium and barium. Typically, the further element is present in the catalyst in a quantity of from 0.01 to 500 mmole/kg, more typically from 0.05 to 100 mmole/kg, calculated as the element on the total

catalyst. Where possible, the further element may suitably be provided as an oxyanion, for example, as a perrhenate, sulfate, nitrate, nitrite, borate or molybdate, in salt or acid form. Salts of Group IA

5   metals or Group IIA metals are suitable.

Preferably, the silver-containing catalyst is one which, when operated fresh, exhibits at 260 °C a theoretical selectivity at zero oxygen conversion, S_0, of at least 6/7 or 85.7 mole-%, more preferably 88 mole-%,

10   most preferably 89 mole-%. The value of S_0 for a given catalyst is found by operating the catalyst at 260 °C in a range of oxygen conversions, resulting in a range of selectivity values S corresponding to the range of oxygen conversions. These values S are then extrapolated back

15   to the theoretical value of S at zero oxygen conversion, by the use of conventional curve-fitting algorithms.

Preferred supported highly selective silver-containing catalysts to be used in the present invention are rhenium-containing catalysts. Such catalysts are

20   known from US-A-4766105 and US-A-4761394, which are incorporated herein by reference. Broadly, these catalysts contain a catalytically effective amount of silver, a promoting amount of rhenium or compound thereof, a promoting amount of at least one further metal

25   or compound thereof and optionally a co-promoting amount of a rhenium co-promoter selected from tungsten, molybdenum, chromium, sulfur, phosphorus, boron, and compounds thereof. More specifically the at least one further metal of these rhenium-containing catalysts

30   is/are selected from the group of Group IA metals, Group IIA metals, titanium, hafnium, zirconium, vanadium, thallium, thorium, tantalum, niobium, gallium and germanium and mixtures thereof. Preferably the at least one further metal is/are selected from the Group IA

metals such as lithium, potassium, rubidium and cesium and/or from the Group IIA metals such as calcium and barium. Most preferably it is lithium, potassium and/or cesium.

5   Preferred amounts of the components of these rhenium-containing catalysts are, when calculated as the element on the total catalyst:

- silver from 10 to 500 g/kg, more preferably from 10 to 400 g/kg,

10   - rhenium from 0.01 to 50 mmol/kg,

- further metal or metals from 10 to 3000 mg/kg, and

- optional rhenium co-promoter from 0.1 to 10 mmol/kg.

More preferably, the rhenium content of these catalysts is at least 0.5 mmole/kg, in particular at

15   least 1.0 mmole/kg, more in particular at least 1.5 mmole/kg, when calculated as the element on the total catalyst. More preferably, the rhenium content of these catalysts is at most 40 mmole/kg, when calculated as the element on the total catalyst. Alternatively, the

20   rhenium content of these catalysts, expressed relative to the surface area of the support, is preferably at least 0.0005 mmole/m^2, in particular at least 0.001 mmole/m^2, more in particular at least 0.0015 mmole/m^2. Preferably the rhenium content of these catalysts is at most

25   0.1 mmole/m^2, more preferably at most 0.05 mmole/m^2, relative to the surface area of the support.

As used herein, the quantity of Group IA metal present in the catalysts is deemed to be the quantity in so far as it can be extracted from the catalysts with de-

30   ionized water at 100 °C. The extraction method involves extracting a 10-gram sample of the catalyst three times by heating it in 20 ml portions of de-ionized water for 5 minutes at 100 °C and determining in the combined extracts

the relevant metals by using a known method, for example atomic absorption spectroscopy.

As used herein, the quantity of Group IIA metal present in the catalysts is deemed to the quantity in so far as it can be extracted from the catalysts with 10 %w nitric acid in de-ionized water at 100 °C. The extraction method involves extracting a 10-gram sample of the catalyst by boiling it with a 100 ml portion of 10 %w nitric acid for 30 minutes (1 atm., i.e. 101.3 kPa) and determining in the combined extracts the relevant metals by using a known method, for example atomic absorption spectroscopy. Reference is made to US-A-5801259, which is incorporated herein by reference.

The olefin oxide produced may be recovered by using methods known in the art, for example by absorbing the olefin oxide in water and optionally recovering the olefin oxide from the aqueous solution by distillation. At least a portion of the aqueous solution containing the olefin oxide may be applied in a subsequent process for converting the olefin oxide into a 1,2-diol, a 1,2-diol ether or an alkanolamine.

The olefin oxide produced in the epoxidation process may be converted into a 1,2-diol, into a 1,2-diol ether or into an alkanolamine.

The conversion into the 1,2-diol or the 1,2-diol ether may comprise, for example, reacting the olefin oxide with water, suitably using an acidic or a basic catalyst. For example, for making predominantly the 1,2-diol and less 1,2-diol ether, the olefin oxide may be reacted with a ten fold molar excess of water, in a liquid phase reaction in presence of an acid catalyst, e.g. 0.5-1.0 %w sulfuric acid, based on the total reaction mixture, at 50-70 °C at 1 bar absolute, or in a gas phase reaction at 130-240 °C and 20-40 bar absolute,

preferably in the absence of a catalyst. If the
proportion of water is lowered the proportion of 1,2-diol
ethers in the reaction mixture is increased. The 1,2-
diol ethers thus produced may be a di-ether, tri-ether,

5   tetra-ether or a subsequent ether. Alternative 1,2-diol
ethers may be prepared by converting the olefin oxide
with an alcohol, in particular a primary alcohol, such as
methanol or ethanol, by replacing at least a portion of
the water by the alcohol.

10   The conversion into the alkanolamine may comprise
reacting the olefin oxide with an amine, such as ammonia,
an alkyl amine or a dialkylamine. Anhydrous or aqueous
ammonia may be used. Anhydrous ammonia is typically used
to favour the production of monoalkanolamine. For

15   methods applicable in the conversion of the olefin oxide
into the alkanolamine, reference may be made to, for
example US-A-4845296, which is incorporated herein by
reference.

The 1,2-diol and the 1,2-diol ether may be used in a

20   large variety of industrial applications, for example in
the fields of food, beverages, tobacco, cosmetics,
thermoplastic polymers, curable resin systems,
detergents, heat transfer systems, etc. The alkanolamine
may be used, for example, in the treating ("sweetening")

25   of natural gas.

Unless specified otherwise, the organic compounds
mentioned herein, for example the olefins, 1,2-diols,
1,2-diol ethers, alkanolamines and organic halides, have
typically at most 40 carbon atoms, more typically at most

30   20 carbon atoms, in particular at most 10 carbon atoms,
more in particular at most 6 carbon atoms. As defined
herein, ranges for numbers of carbon atoms (i.e. carbon
number) include the numbers specified for the limits of
the ranges.

Having generally described the invention, a further understanding may be obtained by reference to the following examples, which are provided for purposes of illustration only and are not intended to be limiting

5 unless otherwise specified.

EXAMPLE 1 - 5 (Example 1 for comparison, Examples 2-5 according to the invention)

A catalyst as defined in US-A-4766105, containing silver, rhenium and rhenium co-promoter and having in the

10 fresh state a theoretical selectivity S_0 at 260 °C of 93%, was used to produce ethylene oxide from ethylene and oxygen. To do this, 2.1-g samples of the crushed catalyst (0.8-1.4 mm) were each loaded into a stainless steel U-shaped tube. The tube was immersed in a molten

15 metal bath (heat medium) and the ends were connected to a gas flow system. The flow rate of the feed was adjusted to give a gas hourly space velocity of 15,200 Nl/(l.h), as calculated for uncrushed catalyst. The flow rate was 35.7 Nl/h. The inlet pressure was 1450 kPa.

20 The feed passed through the catalyst bed in a "once-through" operation consisted of ethylene, oxygen, 3 mole-% carbon dioxide, 2.0 to 6.0 ppmv ethyl chloride and balance nitrogen. In each Example different contents of olefin and oxygen were chosen, and such that the oxygen

25 content was the maximum considered to be allowable avoiding conditions of flammability.

The initial reactor temperature was 225 °C and this was ramped up at a rate of 10 °C per hour to 245 °C and then adjusted so as to achieve a constant ethylene oxide

30 content of 2 mole-% in the outlet stream. For each of the ethylene/oxygen contents combinations, the ethyl chloride content of the feed was varied to identify and then apply the level that provided the optimum selectivity.

The initial performance data of the catalyst (Table I) were obtained when the catalysts had been on stream for a total of at least 1-2 days.   A lower reaction temperature needed to accomplish a certain ethylene oxide

5   content in the outlet stream is indicative for a higher activity of the catalyst.

TABLE   I

Example	Ethylene in feed (mole-%)	Oxygen in feed (mole-%)	Selectivity (mole-%)	Activity ($^{\circ}$C)
1 [1])	25	8.3	85.5	290
2 [2])	30	8.0	86	289
3 [2])	35	7.6	87.5	283
4 [2])	40	7.2	87.5	283
5 [2])	45	6.8	88	280
[1]) comparative [2]) invention				

EXAMPLES 6-10 (for comparison)

10   The procedure as outlined for Examples 1-5 was repeated, except that the gas hourly space velocity was 4,100 Nl/(l.h), as calculated for uncrushed catalyst, and that the flow rate was 9.6 Nl/h.

The initial performance data of the catalyst (Table

15   II) were obtained when the catalysts had been on stream for a total of at least 1-2 days.

TABLE II

Example	Ethylene in feed (mole-%)	Oxygen in feed (mole-%)	Selectivity (mole-%)	Activity (°C)
6 [1])	25	8.3	90	250
7 [1])	30	8.0	89.5	249
8 [1])	35	7.6	90	250
9 [1])	40	7.2	90.5	250
10 [1])	45	6.8	90.5	251
[1]) comparative				

A comparison of Examples 2-5 (according to the invention) with Comparative Example 1 shows that when the process is operated at a high temperature, i.e. above 255 °C, the activity of the catalyst becomes progressively higher when the olefin content of the feed is progressively increased to values above 25 mole-%, despite the fact that the content of the other reactant in the feed, oxygen, is decreased. In addition, a gain in selectivity is achieved. Comparative Examples 6-10 show that a similar increase in activity is not seen when the process is operated at a lower temperature. Instead, the activity tends to decrease with increasing olefin content.

EXAMPLE 11 (according to the invention)

The procedure as outlined for Examples 1-5 was repeated, except that the oxygen content of the feed was 8 mole-%, the gas hourly space velocity of 16,500 Nl/(l.h), as calculated for uncrushed catalyst, the flow rate was 38.6 Nl/h, and the ethylene oxide content in the outlet stream was 1.8 mole-%. Further, the decline in catalyst performance was measured over a time period providing a cumulative ethylene oxide (EO)

production of 1800 kmole/m^3. Then the ethylene content in
the feed was increased to 45 mole-%, with unchanged
oxygen content, and again the decline in catalyst
performance was measured over a time period providing a
5   cumulative ethylene oxide production of 1800 kmole/m^3.

The results have been given in Table III.

Example 11 (according to the invention) shows that
when the process is operated at a high temperature, i.e.
above 255 °C, the catalyst maintains it performance better
10   as the olefin content in the feed is higher.

TABLE III

Ethylene in feed (mole-%)	Selectivity (mole-%)	Activity (°C)	Selectivity decline after 1800 kmole/m³ EO production, (mole-%)	Activity decline after 1800 kmole/m³ EO production, (°C)
30	86.5	278	1.5	10
45	88	270	0.5	0